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TRENDS IN DEVELOPMENT OF ACETYLENE CHEMISTRY IN USSR

[Comment: The development in the USSR of a chemical industry based on acetylene during the period 1950-1953 is discussed in this report.

Numbers in parentheses refer to appended sources.]

Introduction

Although the results in the field of acetylene chemistry and technology reported by USSR investigators parallel, to some extent, German developments in this field which took place during World War II, they partly antedate these developments (cf. investigations by N. D. Zelinskiy, A. Ye. Favorskiy, and S. V. Lebedev) or supplement them (cf. investigations by I. N. Nazarov, N. F. Shostakovskiy, and V. V. Tatarinov). The shortage of liquid fuel in Germany, which led to the hydrogenation of coal, gasification of coal followed by the Fischer-Tropsch process, and low-temperature carbonization to produce liquid fuel as a part of the effort to make Germany self-sufficient in war-time, created the necessity of providing a supply of chemical raw materials for plastics, solvents, synthetic fibers, elastomers, and other products which would be independent both of the nonexistent supply of crude petroleum and the supply of coal-tar-distillation products that was reduced because of diversion of the primary raw material to other uses. This necessity stimulated the development of acetylene chemistry in Germany.

The development of a chemical industry based on acetylene in the USSR must be due to other causes, because rich deposits of crude petroleum exist in that country and are being exploited. One of the causes is presumably the rapid expansion of crude petroleum production in the USSR under the Fifth Five-Year Plan and the availability of large quantities of methane in connection with the expanded production and conversion of crude petroleum. Another may be seen in

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the construction of hydroelectric plants and the resultant availability of cheap electric power both for the production of calcium carbide and the conversion of methane to acetylene by the electric arc method. One may note in this connection that some of the newer hydroelectric developments are in close proximity or relatively close proximity to natural gas fields supplying methane (e.g., the Tsimlyanskaya and Stalingrad hydroelectric-power stations and the Saratov natural gas field). The emphasis in recent USSR work, as far as production of acetylene is concerned, is definitely on the conversion of methane.

In connection with the application of the Tatarinov method of cracking high-molecular hydrocarbons to acetylene in the liquid phase by means of an electric arc, one must bear in mind that catalytic cracking is being used in the USSR on a limited scale only. On the other hand, the capacity of the USSR petroleum industry for aromatization by the pyrolysis method is large. Because of the composition of USSR crudes and because of the relative increase in the number of engines other than those of the carburetor type, the emphasis at present is on the production of diesel fuel and jet fuels. Aromatic constituents of the high and middle boiling range, which must form in considerable quantities as a result of subjecting the appropriate fractions of some crudes to the pyrolysis process (45-47% of tar are formed in pyrolysis), are not suitable for use as diesel or turbojet fuel. However, they ought to be well suited for cracking to acetylene by the Tatarinov method, with some light gasoline forming as a by-product. The same considerations apply to shale oil rich in phenols and to some other crude materials available in the USSR. Acetylene in turn can be used as a starting material for the synthesis of special diesel fuel, gas turbine fuels, and synthetic lubricating oils possessing desirable characteristics. This possibility is envisaged by A. D. Petrov and has been reflected in work done by him and his group.

Various Processes Described

The latest edition of the Large Soviet Encyclopedia (article on "Acetylene"), in addition to outlining the properties of acetylene, its production from calcium carbide, and its uses in welding and as an illuminating gas, summarizes the applications of acetylene as a chemical crude material. After discussing the M. G. Kucherov-K. A. Hofmann reaction (conversion of acetylene into acetaldehyde with the aid of mercury salts) and its industrial applications, the production of vinyl chloride and vinyl acetate from acetylene by reacting this substance in the presence of mercury salts with hydrogen chloride and acetic acid, respectively, the use of vinyl chloride and vinyl acetate as starting materials in the manufacture of plastics, and the manufacture of acetone from acetylene (by a catalyzed reaction of acetylene with water vapor at an elevated temperature), the Large Soviet Encyclopedia states that upon interacting acetylene with alcohols at elevated temperatures and pressures according to the method of A. Ye. Favorskiy and M. F. Shostakovskiy, vinyl ethers are obtained which on polymerization form substances that are used in various fields of technology.

The industrial synthesis of vinylacetylene [by duPont's method] and the conversion of this substance into chloroprene are then discussed. The article in the encyclopedia goes on to say that I. N. Nazarov, who has been awarded the Stalin Prize on two occasions (1942 and 1946), has obtained from acetylene polymerizable oxygen-containing substances which are capable of forming films. The encyclopedia adds that work in this field is of great theoretical and practical importance and concludes the article by saying that, thanks to research done by A. Ye. Favorskiy, N. D. Zelinskiy, A. N. Nesmeyanov, A. D. Petrov, I. N. Nazarov, A. L. Klebanskiy, and many other Soviet scientists, acetylene chemistry is becoming a major field of organic chemistry and technology, the importance of which for the economy of the USSR is constantly increasing.

In the section on the manufacture of acetylene, the encyclopedia says that the production of this substance by the thermal decomposition of natural gas and petroleum products is acquiring industrial importance.(1)

Elsewhere in the encyclopedia (under "Vinylacetylene") it is stated that I. N. Nazarov, by starting with vinylacetylene and applying Favorskiy's reaction, obtained in work begun in 1935 a number of new organic substances including vinylethinylcarbinols, glycols of the vinylacetylene series, and ethers and esters derived from vinylethinylcarbinols. The encyclopedia adds that the substances synthesized by Nazarov serve as starting materials for the production of high polymers and for the synthesis of organic substances of a complicated structure such as hormones, etc.(2)

I. N. Nazarov's work was reviewed briefly in Izvestiya Akademii Nauk SSSR on the occasion of Nazarov's election to an active membership in the Academy of Sciences USSR.(3)

The article on vinylacetylene in the encyclopedia also says that S. V. Lebedev has developed a number of methods for the conversion of vinylacetylene (the dimer of acetylene) into butadiene by hydrogenation.(2)

According to D. N. Andreyev, another method of synthesizing butadiene from acetylene has been developed by A. A. Balandin, Ya. T. Eydus, and Ye. M. Terent'yeva, who demonstrated that acetylene can be converted directly into butadiene by subjecting it to a high-frequency corona discharge. Andreyev states that subsequent work established that the yield of butadiene is improved if the acetylene is diluted with hydrogen or, still better, with ethylene. According to Andreyev, an 18% yield of butadiene can be obtained by this method if a mixture containing 26% of acetylene and 71.3% of ethylene is used.(4)

The hydropolymerization of acetylene has been studied by L. I. Antsus and A. D. Petrov. They found that ethylene freshly formed by the hydrogenation of acetylene undergoes dimerization readily, forming n-butene under some conditions and isobutene under others. They furthermore demonstrated that when acetylene-hydrogen mixtures are converted at a pressure of 25 atmospheres and the low temperatures of 35° with the aid of a nickel-zinc chloride catalyst, the hydropolymerization of acetylene which takes place under these conditions leads predominantly to the formation of branched olefins. They also found that when the process of hydropolymerization is interrupted by adding halides of metals of the second or third group to the nickel, the dimer fraction at which polymerization stops under these conditions consists almost exclusively of isobutene. (9)

Petrov and Antsus (and also the British investigator Sheridan) found that when pure nickel is used as a catalyst, polymerization of acetylene under atmospheric pressure does not take place at all in the absence of hydrogen. The process of polymerization [or more correctly of hydropolymerization] begins only when no less than one fifth of a gram-molecule of hydrogen has been added per gram-molecule of acetylene.(10)

In connection with a discussion of the dependence between the constitution of hydrocarbons and their properties as components of diesel fuel, Petrov has considered the hydropolymerization of diolefins, particularly butadiene, with the view of synthesizing on a practically useful scale branched paraffins which have desirable characteristics as fuels and/or fuel components. He states that this type of synthesis will be much closer to practical realization if the transformations that occur during the conversion can be reduced to the single-stage reactions of hydropolymerization taking place under the conditions of heterogeneous catalysis, i.e., the synthesis can be carried out under conditions resembling those which exist during the hydropolymerization of acetylene.(11)

According to Andreyev, Petrov and Antsus demonstrated that motor fuels of high quality can be obtained by subjecting acetylene-hydrogen mixtures to low-temperature polymerization.(5)

A. D. Petrov discusses in detail the hydrogenation of acetylene to ethylene, German work on the production of lubricating oils by the polymerization of ethylene, and the work of his own group on the subject.(12)

According to A. A. Petrov, who first describes the catalytic hydrogenation of diacetylene to butadiene on the basis of US and German patents, the hydrogenation of vinylacetylene has been studied in detail by S. V. Lebedev and A. L. Klebanskiy. A. A. Petrov states that according to the data obtained by Russian chemists, hydrogenation of vinylacetylene with the aid of a palladium catalyst leads to a mixture of butadiene, butenes, and butane. He further says that according to Zelinskiy, use of nickel [in this reaction] promotes the formation of butane, and adds that the best results [as far as formation of butadiene is concerned] are obtained by electrolytic hydrogenation or hydrogenation with nascent hydrogen. In further reference to the synthesis of butadiene, A. A. Petrov says that the condensation of ethylene with acetylene is one of the earliest methods that has been applied for the preparation of butadiene and that, notwithstanding the fact that nobody has obtained high yields of butadiene as yet by applying this method, continued work on the reaction in question is being done. He adds that published articles and patents on the subject propose various catalysts and conditions for the synthesis which make it possible to bring the yield of butadiene up to 30% without recyclization and up to 85% with recyclization.(13)

The polymerization of acetylene-ethylene mixtures by an electric discharge to obtain vinylacetylene which would polymerize and on addition of hydrogen chloride form chloroprene rubber is discussed by D. N. Andreyev on the basis of US work. According to Andreyev, the polymerization of acetylene-butene-1 mixtures by means of a silent discharge was investigated by A. D. Petrov and Andreyev himself. The product obtained by these investigators was a mixture consisting of olefinic and acetylenic hydrocarbons. This product was found to harden readily and to possess good film-forming properties.(6)

In regard to methods for the industrial production of acetylene, Andreyev says that production from calcium carbide is the method which is principally used at present. He also says that the electric arc method, which has been developed during the past 10-15 years, is another procedure which is suitable for the production of acetylene and that the crude materials for the conversion to acetylene by this method comprise various gases which contain methane (natural gas, by-product gas of hydrogenation plants, etc.) and also, according to recent reports, liquid fuel (i.e., individual petroleum fractions). Andrayev adds that the USSR investigators N. P. Bozhko, S. S. Vasil'yev, Ye. N. Yeremin, N. I. Kobozev, D. K. Koller, and others have participated actively in the development of the electric arc method and have proven by their work that this method for the production of acetylene is capable of competing successfully with the carbide method. After discussing in detail USSR, German, US, Japanese, and other work on the production of acetylene by the electric arc method, Andreyev concludes his discussion by saying that this process proved feasible from the cost standpoint because the principal by-products and secondary products of the process (carbon black, hydrogen, hydrogen cyanide, ethylene, diacetylene, and a number of homologs of acetylene and diacetylene) were utilized, thus reducing the cost of the main product, i.e., acetylene.(7)

Andreyev also gives an account of USSR work on the conversion of liquid petroleum fractions to acetylene by the electric arc method. In describing V. V. Tatarinov's procedure (1934) for the liquid phase cracking of petroleum fractions, coal tar, peat tar, shale oil and tar, etc., to acetylene by means

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of an electric arc, Andreyev says that the best results were achieved by using as raw material diesel fuel or crude petroleum from which the gasoline fraction had been removed. He states that carbon black and hydrogen are the principal by-products of Tatarinov's process. He gives a flowsheet of the Tatarinov process (in which light hydrocarbons of the gasoline range are indicated as one of the products) and describes the results obtained by A. F. Dobryanskiy and A. D. Kokurin, who investigated the application of Tatarinov's method to the conversion of (a) straight run kerosene (b p above 191°), (b) shale tar (b p above 200°) containing 35% of pitch, (c) shale diesel fuel (b p 225-325°) containing up to 24% of phenols and 2.7% of sulfur, (d) peat generator tar (b p above 200°) containing up to 4% of water and 5% of carbon dust, and (e) oil semi-goudron.

According to Andreyev, Dobryanskiy and Kokurin found that 100 g of kerosene, when treated by Tatarinov's method, yield 25.4 g of carbon black and 72.3 g of a gas containing 34.0% of acetylene, 49.0% of hydrogen, 5.5% of methane, 7.5% of ethylene, 3.0% of hydrocarbons of the C_3-C_4 fraction, and 0.6% of carbon monoxide. Andreyev states that according to Dobryanskiy and Kokurin the nature of the crude material does not affect the yield of acetylene and the composition of the gas in general. To confirm this statement, he tabulates the results obtained by these investigators on the five types of crude material used by them. He also states that the production of 1 cubic meter of pure acetylene by the Tatarinov method requires 10-11 kilowatt-hours as compared with the 14 kilowatt-hours needed in the Contardi-Air Liquide process and the 12 kilowatt-hours needed in the carbide process, while the Tatarinov process is simpler than that based on the decomposition of carbide, requires lower capital expenditures, and makes possible the use of transportable installations with the aid of which locally available crude material can be converted. Andreyev then discusses in considerable detail the Contardi-Air Liquide process, outlines research on the generation of acetylene by the electric arc liquid-phase cracking method done by S. Roginskiy-A. Shekhter (who used mazut and anthracene oil in some of their experiments), and draws the conclusions which are summarized below:

Cracking of hydrocarbons in the liquid phase by means of electric discharges results in a gas which has a higher acetylene content (30-40%) than that achieved by subjecting methane to electric discharges (11-13%). For that reason liquid phase cracking by the electric discharge method is preferrable. It follows from the experimental data obtained by E. G. Linder and A. Davis (Journal of Physical Chemistry, Vol 35, p 3649, 1931) that the concentration of acetylene in the gases which are formed is determined exclusively by the structure of the initial hydrocarbons. Polycyclic aromatic hydrocarbons such as naphthalene, biphenyl, phenanthrene, anthracene, acenaphthene, etc., yield gas which is particularly rich in acetylene. One may expect that a high proportion of acetylene will also be contained in the gases obtained by the electric cracking of the simplest homologs of the hydrocarbons mentioned above and substances which are close to them in composition and constitution, particularly compounds containing oxygen and nitrogen such as higher phenols, derivatives of furan, benzofuran and its homologs, diphenyloxide, carbazole, homologs of quinoline and acridine, etc. All of these compounds, including the hydrocarbons mentioned above, are constituents of various tars (coal tar, shale tar, and peat tar) which are commonly used as crude material in the production of acetylene by liquid-phase cracking with the use of electric discharges. The fact that higher yields of acetylene are obtained from aromatic hydrocarbons is in agreement with theoretical calculations reported in Roginskiy and Shekhter's work. Thermochemical calculations show that the production of acetylene from aromatic compounds offers the most advantageous conditions from the standpoint of energy expenditure.

The differences in the concentrations of acetylene obtained by treating methane and liquid crude materials, respectively, are due to differences in the crude material used. When the same type of [suitable] crude material is converted by methods as different as the Tatarinov procedure and the Air Liquide method, good yields of acetylene are obtained in both cases.

At the end of his discussion of the production of acetylene by electric cracking in the liquid phase, Andreyev says that by cracking under appropriate conditions tars that contain nitrogen and oxygen compounds, it ought to be possible to produce in addition to acetylene hydrogen cyanide, aldehydes, alcohols, acids, amines, and other technically valuable compounds.(8)

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